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A comprehensive review of direct borohydride fuel cells

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ABSTRACT

A direct borohydride fuel cell (DBFC) is a device that converts chemical energy stored in borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. Usually, a DBFC employs an alkaline solution of sodium borohydride ($NaBH_4$) as fuel and oxygen or hydrogen peroxide as oxidant. DBFC has some attractive features such as high open circuit potential, ease of electro-oxidation of BH_4^- on non-precious metals such as nickel, low operational temperature and high power density. The DBFC is a promising power system for portable applications. This article discusses prominent features of DBFC, reviews recent developments in DBFC research, and points out future directions in DBFC research.

Contents

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1. Introduction

Fuel cells constitute an attractive class of renewable and sustainable energy sources alternative to conventional energy sources such as petroleum that has finite reserves. Energy generation from petroleum oil and natural gas through combustion in a heat engine being subject to Carnot Cycle limitation is inherently inefficient and is accompanied with environmental pollution. In contrast, a fuel cell is intrinsically energy efficient, non-polluting, silent, and reliable. In some embodiments, it is a low temperature device that provides electricity instantly upon demand, and exhibits a long operating life. Energy efficiencies of about 50–70% can be achieved with fuel cells. Fuel cells combine the advantages of both combustion engines and batteries, at the same time eliminating the major drawbacks of both. Similar to a battery, a fuel cell is an electrochemical energy device that converts chemical energy into electricity and akin to a heat engine, a fuel cell supplies electricity as long as fuel and oxidant are supplied to it.

Among the various types of fuel cells developed so far, polymer electrolyte fuel cells (PEFCs) have the advantage of high power densities at relatively low operating temperatures ($\leq$80 °C) [1] and therefore are considered promising power sources for portable and residential applications. Research and development on PEFCs using hydrogen as the fuel have progressed enormously but their successful commercialization is restricted because of poisoning of platinum anode by carbon monoxide while using a reformer in conjunction with the PEFC and the safety and storage efficiency of the flammable hydrogen gas [2,3]. In order to overcome these difficulties, liquid methanol is used instead to fuel PEFCs. Direct use of liquid fuel in a PEFC simplifies the engineering issues, thereby driving down the system complexity and hence cost. PEFCs that are fed with methanol as fuel are referred to as direct methanol fuel cells (DMFCs). However, DMFCs have limitations of inefficient methanol electro-oxidation, low open circuit potential, and methanol cross-over from anode to cathode compartment [3,4].

The problems arising from the use of methanol in DMFCs can be overcome by using other hydrogen carrying materials such as various borohydride compounds as fuel. Sodium borohydride ($NaBH_4$), which has a capacity value of 5.67 Ah g^{-1} and a hydrogen content of 10.6 wt.% [5–7], is a good alternative to methanol as a fuel. A PEFC that utilizes a borohydride compound, usually sodium borohydride in aqueous alkaline medium, directly as a fuel is termed as direct borohydride fuel cell (DBFC). A schematic diagram of a direct borohydride fuel cell employing oxygen, air, or hydrogen peroxide as oxidant and a cation exchange membrane (CEM) as electrolyte is depicted in Fig. 1. As evident from the figure, the membrane not only serves the important purpose of ion transfer but also functions as a separator between anode and cathode compartments.

Although the concept of DBFC was first demonstrated by Indig and Snyder [8] in the early 1960s, Amendola et al. were the first to report [5] a direct borohydride–air fuel cell that employed an anion exchange membrane (AEM) as electrolyte and exhibited a maximum power density of 60 mW cm^{-2} at 70 °C. The DBFC reported by Amendola et al. [5] could utilize about seven out of a theoretically maximum eight electrons, exhibiting high fuel utilization efficiency. DBFCs are considered attractive energy suppliers, especially for portable applications. DBFC supersedes DMFC in terms of capacity value, electrochemical activity, theoretical open circuit voltage (1.64 V for DBFC employing oxygen as oxidant as against 1.21 V for DMFC using O_2 as oxidant) and power performance at ambient temperature. In addition, use of alkaline electrolytes which feature relatively low corrosion activity, opens up the possibility of applying readily available and low-cost non-precious metal anode catalysts. Both BH_4^- and its oxidation product borate are relatively inert and non-toxic. Borate can be recycled to produce BH_4^- and the techniques involved are under investigations [9]. The present paper reviews previous developments and current status of research in various aspects of DBFC as well as points out the issues that need to be investigated further.

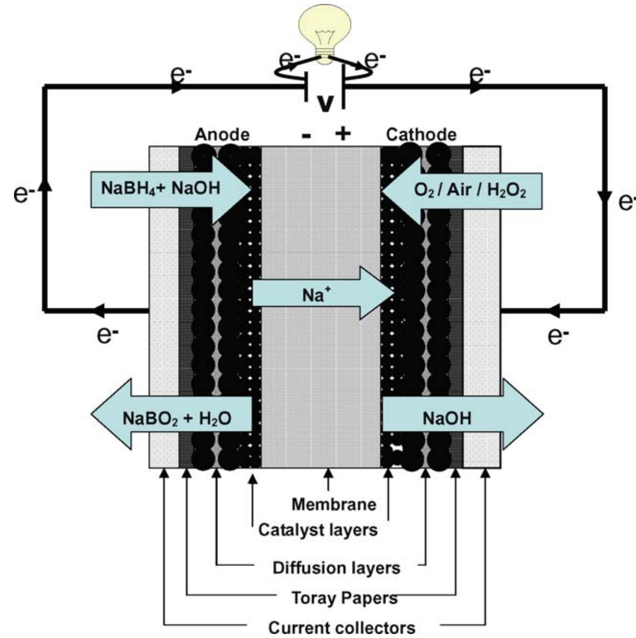


Fig. 1. Schematic diagram of a direct borohydride fuel cell employing oxygen, air or hydrogen peroxide as oxidant.

2. Reactions occurring in DBFC

2.1. Reactions occurring at anode

Borohydride ion, in aqueous alkaline medium, can be oxidized directly on a large variety of electrode materials liberating a maximum of eight electrons. The reaction for the electro-oxidation of BH_4^- is as follows:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (E^{\circ}_{anode} = -1.24\,V\,vs.\,SHE) \qquad (1)$$

A big problem associated with the anodic reaction in DBFC is that BH_4^- hydrolyzes quasi-spontaneously to generate hydroxy borohydride intermediate and hydrogen on various electrode materials [10]. Hydrolysis of BH_4^- takes place through the formation of trihydrohydroxy borate ion intermediate to generate hydrogen [11] as shown in Eqs. (2) and (3):

$$BH_4^- + H_2O \rightarrow BH_3(OH)^- + H_2 \qquad (2)$$

$$BH_3(OH)^- + H_2O \rightarrow BO_2^- + 3H_2 \qquad (3)$$

The presence of atomic hydrogen on DBFC anode makes the anode potential a mixed potential of reactions (1) and (4) and the observed anode potential is between −1.24 and −0.828 V vs. SHE [12].

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad (E^{\circ}_{anode} = -0.828\,V\,vs.\,SHE) \qquad (4)$$

Since hydrogen molecules are formed on the surface of electrodes, it is possible to get them immediately oxidized with the state of the art porous electrodes giving eight electrons provided that BH_4^- hydrolysis does not take place too fast [13].

The detailed mechanism of BH_4^- electro-oxidation is not yet fully understood. However, a possible reaction pathway for electro-oxidation of BH_4^- on platinum electrode is reported in literature [10,14]. Gyenge [15] studied the electrochemical oxidation of BH_4^- on platinum electrode and concluded that BH_4^- undergoes hydrolysis to yield H_2 which is further oxidized at the potential between −0.7 and −0.9 V vs. Ag/AgCl, and the direct electro-oxidation of BH_4^- occurs in the potential range from −0.15 to −0.05 V vs. Ag/AgCl. Mirkin et al. [16] reported that BH_4^- electro-oxidation on gold electrode took place by an electrochemical–chemical–electrochemical reaction mechanism involving unstable intermediates as follows:

$$BH_4^- \leftrightarrow BH_4^{\bullet} + e^- \quad (5)$$

$$BH_4^{\bullet} + OH^- \leftrightarrow BH_3^- + H_2O \quad (6)$$

$$BH_3^- \leftrightarrow BH_3 + e^- \quad (7)$$

The monoborane (BH_3) intermediate then undergoes further reaction to produce a total of eight electrons.

Cheng and Scott [17] studied the kinetics of borohydride electro-oxidation on rotating gold disk electrode. The authors reported that the number of electrons transferred in the borohydride electro-oxidation was around 8 at 0.45 V; the rate constant was between 0.016 and 6.13 cm s^{-1}; the orders of the electro-oxidation reaction with respect to tetrahydroborate and hydroxide ions were 1.0 and 1.1, respectively; the activation energy for borohydride electro-oxidation was 27.0 kJ mol^{-1}. A rotating ring disk electrode study by Krishnan et al. [18] reveals that the electro-oxidation of BH_4^- occurs over a wide potential range of −0.500 to 0.400 V vs. NHE on gold electrode under hydrodynamic conditions and also the extent of $BH_3(OH)^-$ generated increases with increase in anodic polarization of the disc electrode. The authors opined that the increase in the amount of $BH_3(OH)^-$ with increased electrode polarization is a concern with respect to fuel utilization efficiency in DBFC.

The direct oxidation of $NaBH_4$ in concentrated NaOH solution has been studied by Chatenet et al. [19] on silver and gold electrocatalysts. The authors opined that the BH_4^- electro-oxidation mechanism on silver and gold electrodes varies at different $[OH^-]/[BH_4^-]$ ratios. When BH_4^- concentration is low, a negligible amount of BH_3OH^- is produced and the oxidation reaction proceeds without the chemical hydrolysis of BH_4^-. The authors found that the reaction intermediates are all adsorbed at the electrode surface and BH_4^- oxidation mechanism start following the adsorption step (8) and electrochemical step (9):

$$BH_4^- + M \rightarrow BH_{4,ad}^- \quad (8)$$

$$BH_{4,ad}^- + OH^- \rightarrow BH_{3,ad} + H_2O + 2e^- \quad (9)$$

At low $[OH^-]/[BH_4^-]$ ratio, BH_4^- undergoes spontaneous hydrolysis into non-negligible amounts of BH_3OH^- which is further oxidized at very low potential (<−1 V versus NHE). BH_4^- is oxidized at much higher potential (above −0.6 V versus NHE for Au/C and −0.3 V versus NHE for Ag/C). The initial steps of BH_4^- direct oxidation might be much slower than the BH_3OH^- oxidation. In addition, there seems to be a particle size effect for carbon-supported metals since the onset for the oxidation wave is at least 0.1 V lower for the nanoparticles than that for the bulk metals. The state of the electrode surface also plays a role in the tetrahydroborate oxidation reaction. For silver electrodes, surface oxides need to be present to enable the reaction that is not observed for gold electrodes. Nanoparticles have at least 0.1 V lower onset oxidation wave than bulk metals.

Lee et al. [20] studied the mechanism of electro-oxidation of BH_4^- on hydrogen storage alloy and stated that hydrogen releasing agent such as BH_4^- first releases hydrogen and electrons in the aqueous electrolyte solution through electrochemical decomposition and oxidation by the hydrogen storage alloy catalyst according to Eq. (10).

$$BH_4^- + 4OH^- \rightarrow BO_2^- + 2H_2O + 4H + 4e^- \quad (10)$$

The released hydrogen (H) is stored in a hydrogen storage alloy (M) as metal hydride (MH_x); the reaction can be expressed by Eq. (11).

$$M + xH \leftrightarrow MH_x + \text{Heat} \quad (11)$$

Hydrogen stored as metal hydride (MH_x) in the hydrogen storage alloy produces electrons by dehydrogenation of the latter as shown by Eq. (12):

$$MH_x + xOH^- \rightarrow M + xH_2O + xe^- \quad (12)$$

2.2. Reactions occurring at cathode

The cathodic reaction with oxygen as the oxidant is written as:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (E^{\circ}_{cathode} = 0.40\,\text{V vs. SHE}) \quad (13)$$

The mechanism of oxygen reduction reaction is complicated and it involves generation of hydrogen peroxide and metal oxide by-product intermediates that decrease the activity of the electro-catalysts. The net cell reaction for DBFC with oxygen as oxidant is written as:

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O \quad (E^{\circ}_{cell} = 1.64\,\text{V}) \quad (14)$$

Due to the porosity of the membrane, large concentration gradient and electrical potential gradient across the membrane, BH_4^- crosses over from anode to the cathode compartment by diffusion and migration [21]. BH_4^- crossover has a great influence on oxygen reduction reaction (ORR) in the cathode. Chatenet et al. [22] studied the selectivity for ORR in NaOH solution with the presence of $NaBH_4$ for carbon-supported platinum, gold, silver, and manganese oxide electro-catalysts. With sodium borohydride in sodium hydroxide solution, carbon supported Pt, Au, and Ag become less effective for ORR than they are in pure sodium hydroxide solution and the open-circuit potential decreases tremendously. In contrast, manganese oxide-based electro-catalysts show as good intrinsic ORR activity as platinum in pure sodium hydroxide solution and also display significant selectivity for ORR when sodium borohydride is present in sodium hydroxide solution.

The cathodic reaction with H_2O_2 as oxidant is represented by Eq. (15) as shown below.

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (E^{\circ}_{cathode} = 0.87\,\text{V vs. SHE}) \quad (15)$$

In DBFC, H_2O_2 is prone to decomposition at cathode catalyst surface producing oxygen and water as expressed by Eq. (16) shown below.

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (16)$$

The liberated oxygen is further electrochemically reduced at the cathode according to Eq. (13). The net cell reaction for DBFC using H_2O_2 as oxidant is expressed as Eq. (17).

$$BH_4^- + 4H_2O_2 \rightarrow BO_2^- + 6H_2O \quad (E^{\circ}_{cell} = 2.11\,\text{V}) \quad (17)$$

Cathode potential varies with pH of the oxidant [6,23] according to Eqs. (18) and (19) as shown below.

$$E(O_2) = 1.23 - 0.059\text{pH} \quad (18)$$

$$E(H_2O_2) = 1.78 - 0.059\text{pH} \quad (19)$$

As the pH decreases, the rate of H_2O_2 decomposition at the cathode catalyst surface decreases. At lower pH values, the probability of direct electro-reduction of H_2O_2 increases, whereas at higher pH values the possibility of decomposition of H_2O_2 to O_2 followed by the reduction of the latter increases. Direct electro-reduction of H_2O_2 and chemical decomposition of H_2O_2 to O_2 followed by the electro-reduction of the latter in DBFC are expressed as Eqs. (20)–(22), respectively.

$$4H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O \quad (E_c^\circ = 1.78\,V\,vs.\,SHE) \tag{20}$$

$$4H_2O_2 \rightarrow 4H_2O + 2O_2 \tag{21}$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (E_c^\circ = 1.23\,V\,vs.\,SHE) \tag{22}$$

Depending on the pH of H_2O_2 solution, the theoretical OCV varies between 1.64 and 3.02 V [24].

3. Electrode

3.1. Anode catalyst materials

Electro-catalysts such as Ni, Pt, and Pd have good catalytic activity towards both the electrochemical oxidation reaction and the hydrolysis reaction [25–27]. Therefore, DBFCs using these metals as anode give high power density but low faradic efficiencies, e.g., 50% for nickel [25]. Higher fuel efficiencies can be achieved on Pd and Pt electrodes at low BH_4^- concentrations and high anode currents [26]. Catalytic activity of metals such as Au, Pt, Ag, Pd, and Ni towards electro-oxidation of BH_4^- was studied by Çelikkan et al. [28]. The authors have observed that among all the metals studied, Au is the most effective and Ni is the least effective electro-catalyst towards borohydride oxidation. Chatenet et al. [19] have reported that electro-oxidation of BH_4^- yield about 7.5 electrons on gold and silver electrodes in contrast to about 4 electrons on platinum. The high utilization efficiencies of gold and silver towards BH_4^- electro-oxidation are due to their low activity towards hydrolysis of BH_4^-. Nevertheless, gold and silver exhibit slow kinetics towards electro-oxidation of BH_4^-, the former being better than the latter [19]. Amendola et al. [5] and Feng et al. [29] have reported that 6.9 and 7.4 electrons out of a theoretical value of 8 electrons can be utilized on gold electrode, respectively.

Gyenge et al. [27] prepared colloidal Pt, Pt-alloys, and Atwan et al. prepared colloidal Os, Os-alloys [30], Au, Au-alloys [31], Ag, and Ag-alloys [32] by modified Bönneman method and investigated them as electro-catalysts for BH_4^- oxidation. Alloying Au with Pd or Pt was shown to improve the kinetics of borohydride oxidation and higher cell voltage was obtained using Au-Pt than colloidal Au [31]. The particle sizes of colloidal Au is larger than that of Pt and Pd, and therefore by alloying colloidal Au with Pt or Pd, the mean particle size of catalyst is reduced [31]. Yet, further studies are needed to determine whether the particle size effect contributes to the improvement in electrode kinetics of borohydride oxidation in addition to the mechanistic and kinetic effects [31].

Among the non-precious metals, nickel has received maximum importance as catalyst for electro-oxidation of BH_4^- [26]. In fact, Ni has been employed as a catalyst in Sabatier and Senderens reaction [33], which is the oldest method for hydrogenation of unsaturated hydrocarbons probably due to its unique affinity towards adsorption of hydrogen and hydrogen containing unsaturated organic compounds. Moreover, Ni is a major component of hydrogen storage materials such as AB_2 and AB_5-type alloys [23]. It will be useful to understand the origin of this unique affinity of Ni towards hydrogen among all elements belonging to the 3d-series of transition metals. Nickel exhibits more negative OCP and less columbic efficiency than those of Pd. In contrast, Pd shows lesser OCP but higher columbic efficiency than Ni. Thus, mixing Ni powder with Pd tends to enhance fuel cell performance [34]. Ag or Au additions were shown to more effectively depress hydrogen evolution than Pd additions, but these materials degrade the cell performance [35]. A problem with Ni electrode is that it might gradually form stable oxide or hydroxide and so porous Ni electrode gradually increased its polarizations as shown by the stability tests [36].

Some researchers investigated bimetallic Ni–Pt catalyst and showed that they can be superior to the monometallic Ni or Pt catalyst towards borohydride electro-oxidation [27,37,38]. Geng et al. prepared carbon-supported Ni and Ni-Pt alloy catalysts by chemical reduction of $Ni(NO_3)_2$ and a mixture of $Ni(NO_3)_2$ and H_2PtCl_6 with hydrazine respectively and employed them as anode catalysts in DBFCs [37]. Electrochemical measurements showed that Ni–Pt/C had improved electro-catalytic activity and stability than Ni/C catalyst. A maximum power density of 221 mW cm^{-2} was obtained at 60 °C with Ni_{37}-Pt_3/C as the anode catalyst. Although Ag has worse characteristics in terms of kinetics for borohydride electro-oxidation in comparison to Au, carbon supported Ag being a non-precious material is desirable as it gives a reasonably good performance, e.g., 40–50 mW cm^{-2} [39]. Silver exhibits better activity than gold towards the BH_3OH^- direct oxidation and therefore can serve as co-catalyst to efficiently oxidize the by-product of BH_4^- hydrolysis [19]. Feng et al. [40] studied Ag and Ag–Ni alloy anode for DBFCs and found that Ag- and AgNi-based anode could realize direct electro-oxidation of BH_4^- giving more than 7 electrons per BH_4^-. Ag–Ni alloy based-borohydride fuel cells exhibited a higher discharge voltage and capacity than Ag, possibly because of the electro-catalytic activity of Ni towards BH_4^- electro-oxidation and the inhibition effect of Ag towards BH_4^- hydrolysis. Different precious and non-precious metals and metal alloys studied as electro-catalysts for electro-oxidation of BH_4^- by various research groups are summarized in Table 1.

Hydrogen storage alloys are metallic materials that have a unique ability to reversibly absorb and release significant amounts of hydrogen gas. Among the broad variety of hydrogen storage alloys that have been studied so far [41,42], two groups of materials namely, AB_5 and AB_2-type alloys have the most advantageous combination of high hydrogen storage capabilities and operational parameters. It has been reported in the literature [43] that hydrogen holding ability of AB_5-type alloys is better than that of AB_2-type alloys. This is probably the reason for higher power density achieved with AB_5-type than that achieved with AB_2-type hydrogen storage alloy [23]. Because hydrogen storage alloys can absorb large quantities of hydrogen, they are expected to reduce hydrogen evolution in DBFCs. For the Zr-based AB_2 Laves phase alloy, special surface treatment was employed to improve its electrochemical performances [44]. During the procedure, alloys were ball-milled in a complex fluoride solution. The F-treated alloy was found to possess larger specific surface area and a highly Ni-covered surface.

Wang et al. [45] found that $L_mNi_{4.78}Mn_{0.22}$ hydrogen storage alloy exhibited a high electrochemical catalytic activity in both the discharge process and the hydrogen generation process. The same alloy was modified and employed as anode in DBFC by Wang et al. [46]. After modification, both the electrochemical catalytic activity of the electrodes and H_2 generation rate decreased and therefore, fuel utilization efficiency was enhanced. Various AB_5 and AB_2-type hydrogen storage alloys were employed as anode materials in DBFCs and the power performances achieved under various conditions from such DBFCs are given in Table 2. It may be noted that the coulombic efficiency of an anode material towards borohydride electro-oxidation depends not only on material properties of the anode but also on a variety of other experimental

Table 1
DBFC performance data obtained with various metal-based anodes.

Anode electro-catalyst (loading/mg cm^{-2})	Cathode electro-catalyst (loading/mg cm^{-2})	Membrane	Oxidant	Temperature (°C)	Power density (mW cm^{-2})	Ref.
Ni powder (167)	Pt/C (1)	Nafion®-211	Air	25	40	[70]
Ni/C (1)	Pt/C (1)	Nafion®-212	O_2	60	150	[37]
Ni/C (2)	Pt/C (2)	Nafion®-117	O_2	85	40.5	[39]
Pd/C (1.08)	Pt/C (0.30)	Nafion®-117	Air	25	19.4	[84]
Pd/C (2)	Pt/C (2)	Nafion®-117	O_2	85	89.6	[39]
Pt/C(1)	Pt/C (1)	Nafion®-212	O_2	60	100	[37]
Pt/C (2)	Pt/C (2)	Nafion®-117	O_2	85	51.3	[39]
Pt/C (1.3)	Non-platinum catalyst/Ni mesh (NA)	(Morgane® ADP)	Air	RT	200	[38]
Ni + Pd/C (20)	Pt/C (1)	Nafion®-112	Air	60	250	[35]
Ni + Pd/C + Zr–Ni alloy (10)	Co-PPY-C (1.2)	Nafion®-117	Air	ambient	65	[63]
Ni37–Pt3/C (1)	Pt/C (1)	Nafion®-212	O_2	60	221	[37]
Pt–Ni/C (0.8)	Non-platinum catalyst/Ni mesh (NA)	(Morgane® ADP)	Air	RT	115	[38]
Pt–Ru (1)	Pt/C (1)	(Morgane® ADP)	O_2	60	149.33	[83]
Ag/C (2)	Pt/C (2)	Nafion®-117	O_2	85	43.6	[39]
Ag/Ti (2)	Pt/C (2)	Nafion®-117	O_2	85	50	[68]
Au/C (2)	Pd/C(2)	Nafion®-117	O_2	85	65.6	[39]
Au/C (2)	Ag/C(2)	Nafion®-117	O_2	85	32.8	[39]
Au/C (2)	Ni/C(2)	Nafion®-117	O_2	85	35.4	[39]
Au/C (2)	Pt/C (2)	Nafion®-117	O_2	85	72.2	[74]
Au/C (2)	FeTMPP (2)	Nafion®-117	O_2	85	65.3	[55]
Au/Ti (2)	Pt/C (2)	Nafion®-117	O_2	85	81.4	[68]
Au (0.8)	Silver nitrate (NA)	AEM	Air	RT	12	[53]
Au (0.8)	MnO_2 (NA)	AEM	Air	RT	28	[53]
Au–Pt (1)	MnO_2 (NA)	AEM	Air	RT	20	[53]
97% Au + 3% Pt	NA	AEM	Air	70	60	[5]
Au (0.5)	Pt/C (4.0)	Nafion®-117	Acidified H_2O_2	20	37.5	[77]
Pd	Au (0.5)	Nafion®	Acidified H_2O_2	60	680	[65]

NA: Information not available in the cited literature.

factors such as method of preparation of the electrode, catalyst support, etc. This is given in a table in reference [47] that summarizes the number of electrons liberated during electro-oxidation of BH_4^- on a large number of anode materials.

A typical way of making electrode ink is to mix catalyst powders (either carbon supported or unsupported), with/without isopropyl alcohol, and Nafion solution or PTFE suspension as a binder [23,38,48–53]. The ink is then brushed or sprayed on to carbon paper or carbon cloth substrate. Nafion has both hydrophobic and hydrophilic features while PTFE is hydrophobic. Nafion addition was shown to effectively improve ion conductivity in the PEFC and DMFC electrodes. Kim et al. [50] reported that increasing Nafion binder content to 25 wt.% improved cell performance due to reduced interfacial resistance, but a further increase in Nafion weight percent lowered the cell performance, possibly because Nafion, being an electrical insulator lowers electrical conductivity of the electrode. Polarization data recorded as a function of Nafion binder content in the anode catalyst layer DBFCs are shown in Fig. 2. Adding proper amount of Nafion solution to the anode was also found to depress hydrogen evolution [35]. To increase porosity of the anode, Liu et al. [54] used sugar as pore formation agent and Ni foam as substrate. These micropores facilitate the release of hydrogen bubbles from the anode.

3.2. Cathode catalyst materials

Platinum is commonly used as DBFC cathode material, due to its high intrinsic activity for oxygen reduction, high electrical conductivity, and good chemical stability [39]. Cheng et al. prepared various cathode catalysts by impregnation method and studied their activity toward ORR in DBFC [39,55]. Pt/C demonstrated the highest catalytic activity towards ORR and the best

Table 2
Performance data for DBFCs employing AB_5 and AB_2-type hydrogen storage alloy anodes.

Anode catalyst	Cathode catalyst	Oxidant	Membrane	*T* (°C)	Power density (mW cm^{-2})	Ref.
$M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$	Prussian blue	$H_2O_2 + H_2SO_4 + KCl$	Nafion®-117	30	68	[67]
$M_mNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	Cobalt Phthalocyanin	Air	None	RT	90	[60]
$M_mNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$	$PbSO_4$/C	$H_2O_2 + H_2SO_4$	Nafion®-961	25	10	[78]
$M_mNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	Iron Phthalocyanin/C	Air	None	RT	92	[61]
$M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$	FeTMPP/C	$H_2O_2 + H_2SO_4$	Nafion®-117	70	82	[66]
$M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$	$PbSO_4$/C	$H_2O_2 + H_2SO_4$	Nafion®-117	70	120	[66]
$M_mNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$	Au/SS mesh	$H_2O_2 + H_2SO_4$	Nafion®-961	25	50	[79]
$M_mNi_{3.35}Co_{0.75}Mn_{0.4}Al_{0.3}$	MnO_2/C	O_2	None	25	70	[57]
$M_mNi_{4.5}Al_{0.5}$	Pt/C	H_2O_2	Nafion®-117	70	130	[23]
$M_mNi_{3.2}Al_{0.2}Mn_{0.6}Co_{1.0}$	Pt/C	H_2O_2	Nafion®-117	70	100	[23]
$M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$	Pt/C	H_2O_2	Nafion®-117	70	150	[23]
$M_mNi_{3.2}Al_{0.2}Mn_{0.6}B_{0.03}Co_{1.0}$	Pt/C	H_2O_2	Nafion®-117	70	125	[23]
$L_mNi_{4.78}Mn_{0.22}$	Nickel foam	NA	None	–	NA	[45]
$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$	Pt/C	O_2	Nafion®-117	60	NA	[7]
$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$	Pt/C	O_2	Nafion®-117	85	190	[6]
$ZrCr_{0.8}Ni_{1.2}$	Pt/C	O_2 and air	None	RT	NA	[20]
$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$	Metal hydride	NA	Nafion®-117	–	NA	[12]
$Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Cr_{0.05}Co_{0.05}Ni_{1.2}$	Pt/C	H_2O_2	Nafion®-117	70	70	[23]

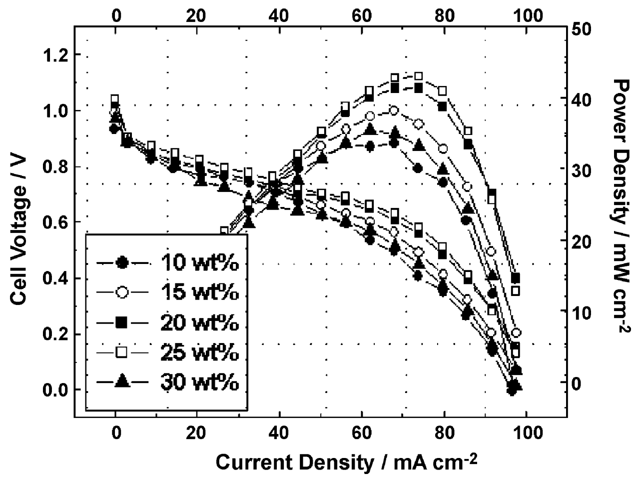


Fig. 2. Polarization data recorded as a function of Nafion binder content in the anode catalyst layer at room temperature for air-breathing mode of DBFCs that employ 6 M KOH as electrolyte and unsupported platinum as both anode as well as cathode catalysts.From Ref. [50].

stability as compared to Pd/C, Ag/C, and Ni/C cathode catalysts [39]. A major concern of using Pt/C for commercial applications is its high cost. Non-precious materials such as iron tetramethoxyphenyl porphyrin (FeTMPP), silver and nickel were studied as cathode electro-catalysts for ORR performances [55]. Among them, FeTMPP showed the best borohydride tolerance and superior performance. Borohydride-oxygen fuel cell using FeTMPP and silver cathodes showed comparable activity and stability to that with the Pt cathode.

Another possible non-precious cathode material is manganese oxide-based electro-catalysts which display sufficient selectivity for ORR and feeble catalytic activity towards electro-oxidation and as well as hydrolysis of sodium borohydride. As a result, the cathode degradation caused by BH_4^- crossover is eliminated [29,52,56,57]. A DBFC based on MnO_2-catalyzed cathode and hydrogen storage alloy anode achieved a peak powder density of 70 mW cm^{-2} at a load current density of 180 mA cm^{-2} operating at a temperature of 25 °C as shown in Fig. 3 and an electron utilization of 7.5 per BH_4^- [57]. Another class of non-noble metal catalysts for ORR are metal phthalocyanines, which have been used in Ni-MH batteries [58], DMFCs [59], and recently in DBFCs [60,61]. Ma et al. [60,61] investigated Cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc) as cathode catalysts for ORR in DBFCs. Electrochemical measurements showed that both electro-catalysts exhibited reasonably good electro-activity for ORR and tolerance towards electro-oxidation of BH_4^-. The DBFC employing CoPc or FePc as cathode catalysts and hydrogen storage alloy anode achieved a peak power density as high as 92 mW cm^{-2} and a good short-term durability over a period of 50 h at ambient condition without an ion exchange membrane separator.

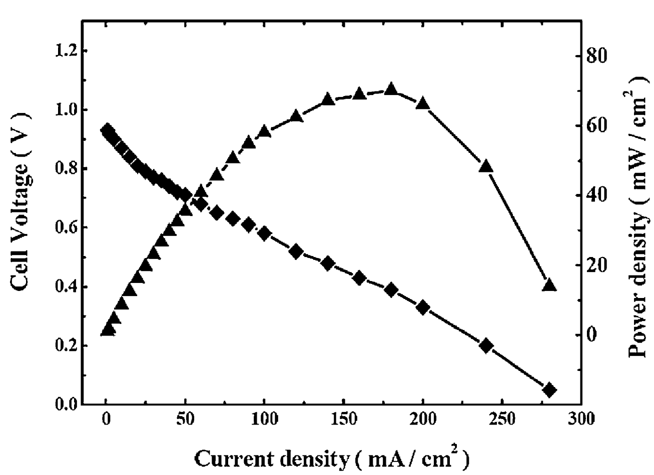


Fig. 3. Electrochemical performance data for a DBFC that employs carbon-supported MnO_2 as cathode and hydrogen storage alloy $M_mNi_{3.35}Co_{0.75}Mn_{0.4}Al_{0.3}$ as anode and an aqueous solution of KBH_4 in KOH as electrolyte recorded at 25 °C.From Ref. [57].

Another metallo-organic compound that is a viable candidate as cathode catalysts in the DBFC is cobalt polypyrrole carbon (Co-PPY-C), which has demonstrated its effectiveness as cathode catalysts in PEFC [62]. In a recent attempt, cobalt polypyrrole carbon (Co-PPY-C) composite was used as cathode catalyst in DBFC and demonstrated a comparable ORR activity to Pt/C and improved stability compared to Ag/C and Pt/C catalyst [63]. Perovskites (ABO_3) have outstanding catalytic activity for ORR in alkaline media, high stability, and good electrical conductivity. Ma et al. [64] prepared carbon-supported $LaNiO_3$ perovskite catalysts by the citrate based sol–gel method and employed them as cathode catalyst for DBFC. A DBFC with $LaNiO_3$/C-catalysed cathode and hydrogen storage alloy-catalyzed anode and no membrane separator exhibited a peak power density of 127 mW cm^{-2} at 65 °C under atmospheric pressure and good performance stability for 500 h. With the usage of these organo-metallic compounds and perovskite-based oxides as cathode materials, which have high selectivity towards ORR and excellent tolerance towards BH_4^- electro-oxidation, probalility of developing mixed-reactant DBFCs that employ no membrane separators and hence cost-effective, is increased.

To find an appropriate metal cathode for direct borohydride–hydrogen peroxide fuel cell, Gu et al. [65] used Pourbaix diagrams as guide and found gold as an effective cathode catalyst, which effectively reduces H_2O_2 yielding high power density, diminishes H_2O_2 decomposition and resists corrosion. However, cost was not considered as a key factor in catalyst selection. The authors employed sputter deposition and electrodeposition methods to deposit cathode catalyst on diffusion layers. Cathodes fabricated by both methods showed higher OCVs and power densities than cathodes fabricated by conventional ink pasting method. Electro-deposition is able to deposit nano-sized catalyst particles where electronic and protonic conductions coexist and therefore catalyst loading is reduced. This method has the advantage of ease of preparation and low cost requirement. The current density affects properties of electrodeposited catalysts, such as particle size, particle shape and distribution. When the current density increases to the limiting value, the performance of the electrode decreases dramatically due to the growth of dendritic crystals and the loss of the deposition layer through the generation of hydrogen [65]. Sputtering deposition has been shown to reduce the catalyst loading as compared to the electro-deposition method while giving almost the same power density. This method allows the preparation of catalysts in nanometer scale with uniform distribution, precise content, thickness, and microstructure morphology. The preparation process is simple and easy to be applied in large scale systems.

To develop low cost cathode catalyst for the electro-reduction of hydrogen peroxide, Raman et al. [66] studied carbon supported iron tetramethoxy phenyl porphyrin (FeTMPP/C) and carbon-supported lead sulphate ($PbSO_4$/C) electrodes and opined that these materials could be possible electro-catalysts for DBFC employing H_2O_2 as oxidant. From cyclic voltammetry studies, the authors have concluded that catalytic activity of FeTMPP towards electro-reduction of H_2O_2 is due to the presence of FeN_4 moiety while that of $PbSO_4$ towards electro-reduction of H_2O_2 is due to Pb(II)/Pb(II + x) redox couple. Polarization data for DBFCs with acidic and alkaline hydrogen peroxide fed at FeTMPP/C cathode are shown in Fig. 4. A maximum power density of

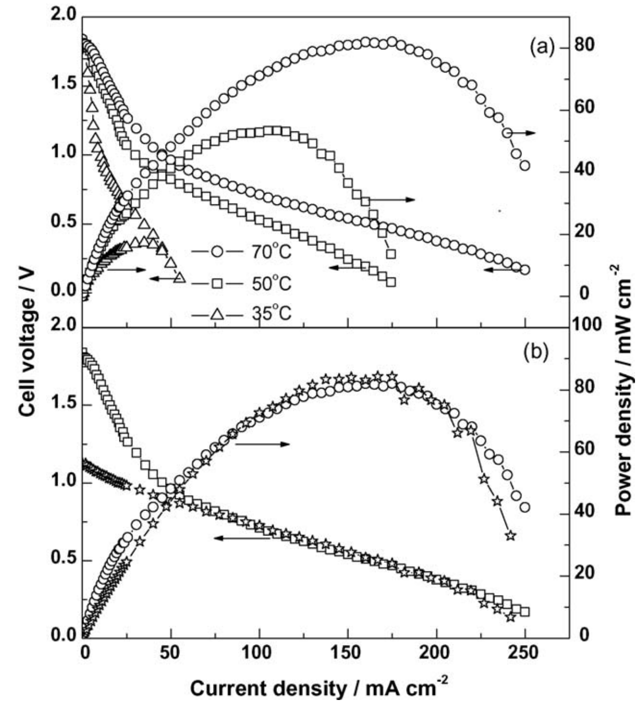


Fig. 4. (a) Cell polarization data for DBFCs employing Nafion®-117 membrane as electrolyte operating at temperatures between 30 and 70 °C with aqueous alkaline solution of $NaBH_4$ fuel fed at $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy anode and 0.5 M H_2O_2 oxidant in 0.5 M sulfuric acid solution fed at the FeTMPP/C cathode, and (b) a comparison of polarization data for similar DBFCs operating at 70 °C with acidic hydrogen peroxide fed at the FeTMPP/C cathode and alkaline hydrogen peroxide fed at the FeTMPP/C cathode at 70 °C.From Ref. [66].

82 mW cm^{-2} at 70 °C was achieved. As shown in Fig. 5, a much higher power density (120 mW cm^{-2}) was achieved with a similar DBFC employing $PbSO_4$/C cathode at the same temperature. Another alternative cost effective cathode material is Prussian Blue (PB). Selvarani et al. [67] employed carbon-supported PB anchored with cetyl-trimethyl ammonium bromide as cathode catalyst in a direct borohydride/hydrogen peroxide fuel cell and achieved a peak power density of 68 mW cm^{-2} at 30 °C.

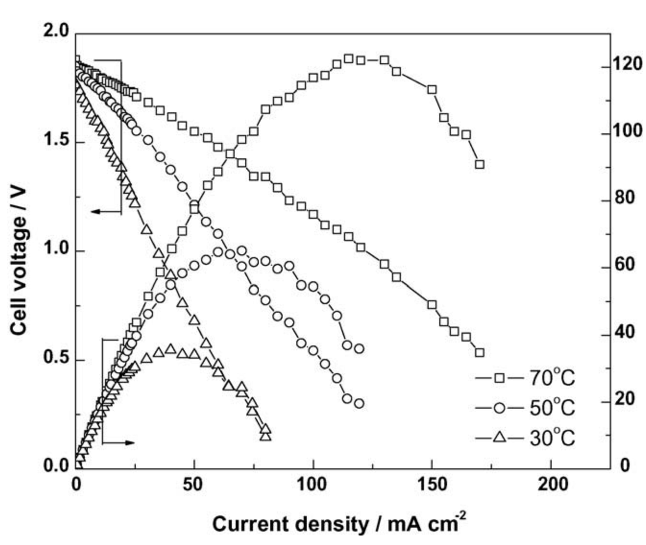


Fig. 5. Cell polarization data for DBFCs employing Nafion-117 membrane as electrolyte operating at temperatures between 30 and 70 °C with aqueous alkaline $NaBH_4$ feed at $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy anode and 0.5 M H_2O_2 in 0.5 M sulfuric acid solution feed at the $PbSO_4$/C cathode.From Ref. [66].

3.3. Catalyst supporting material

Catalyst supporting material has a very important role to play in obtaining high performance of an electrode and hence the cell. It was shown by Kim et al. [50] that the performance of a DBFC employing 1.5 mg cm^{-2} carbon-supported platinum anode is comparable to that of a DBFC employing an unsupported platinum anode with 6 mg cm^{-2} platinum loading. Further, coulombic efficiencies of DBFCs using carbon-supported and unsupported platinum anodes have been found to be 62.3 and 68.1%, respectively. The carbon-supported platinum anode has been found to possess higher catalytic activity and hence, more cost-effective as compared to the unsupported platinum anode. Yet, carbon powder has the disadvantage of poor adhesion and its deposition method is relatively complicated. Activated carbon cloth with a surface area of 2000 m^2 g^{-1} was chosen by Gu et al. [65] as the supporting material for noble metals. High surface area helps to produce smaller catalyst particles and to disperse these particles finely and uniformly on the surface. However, the increase in pore radius reduces electrical conductivity and therefore exerts a negative effect on the fuel cell performance. So, although high surface area is favored for high DBFC performance, there is an optimal activation level for supporting materials.

Titanium mesh was considered by Cheng and Scott [68] as a promising alternative catalyst support due to its merits, such as acceptable electronic conductivity, high chemical and electrochemical stability, open structure, and ease of fabrication. As shown in Fig. 6(a), the DBFCs with the Ti mesh-supported Ag and Au anodes showed superior performances as compared to the DBFCs employing same anodes supported on carbon for all catalyst loadings. Power density as high as 92 mW cm^{-2} and reasonably good stability were obtained for the DBFC employing Au/Ti mesh anode at 85 °C. As shown in Fig. 6(b), cell voltages of DBFCs with Ti mesh-supported anodes are higher than those of DBFCs with carbon-supported anodes for the entire duration of the stability test. Ponce de Léon et al. [69] used titanate nanotubes supported gold as catalyst for electro-oxidation of BH_4^- and it has been found that Au nanoparticles deposited on the nanotubular titanate support carried approximately twice the electrical charge compared to carbon supported Au during the electro-oxidation of BH_4^-.

3.4. Catalyst loading

Catalyst loading is an important factor in determining the DBFC power performance. An increase in catalyst loading would increase performance. However, catalyst utilization has been found to be not proportional to catalyst loadings [39]. An increase in anode loading from 1 to 2 mg Au cm^{-2} resulted in a 15% increase in power density while further increasing the anode loading from 2 to 5 mg Au cm^{-2} led to only 1.4% increase in power density as shown in Fig. 6(a). This is due to the negative effect of the thick catalyst layer on resistance and mass transport [39]. Variation of power performance of a micro DBFC with various Pt loadings in the cathode was examined by Liu et al. [70]. It was found that the power density increased by only 20% when Pt loading in the cathode was increased by about five times while keeping the thickness almost the same. The authors concluded that the DBFC performance was not very sensitive to Pt loading and therefore low Pt loading can be applied to achieve optimum cell performance. Thus, it is clear that optimization of catalyst loading is of utmost importance to achieve maximum output from a DBFC.

3.5. Diffusion layer

Diffusion layer (DL) in PEFCs serves as electronic conductor between bipolar plates and the catalyst layers, functions as a porous

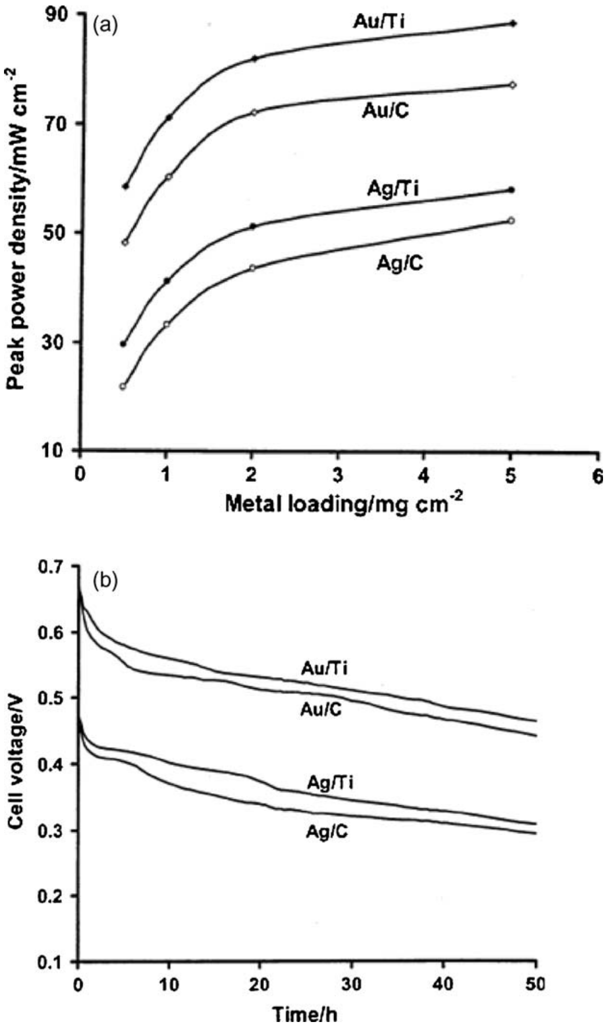


Fig. 6. (a) Data pertaining to the effect of anode catalyst loading on power density of DBFCs that comprise carbon and titanium mesh-supported silver and gold as anodes, carbon-supported platinum as cathode, Nafion®-117 membrane as electrolyte, oxygen as oxidant recoded at 85 °C and at ambient pressure. (b) Data pertaining to the longevity of DBFCs that comprise carbon and titanium mesh-supported silver and gold as anodes, carbon-supported platinum as cathode, Nafion®-117 membrane as electrolyte, oxygen as oxidant recoded at 25 °C and ambient pressure under a load current density of 20 mA cm^{-2}.From Ref. [68].

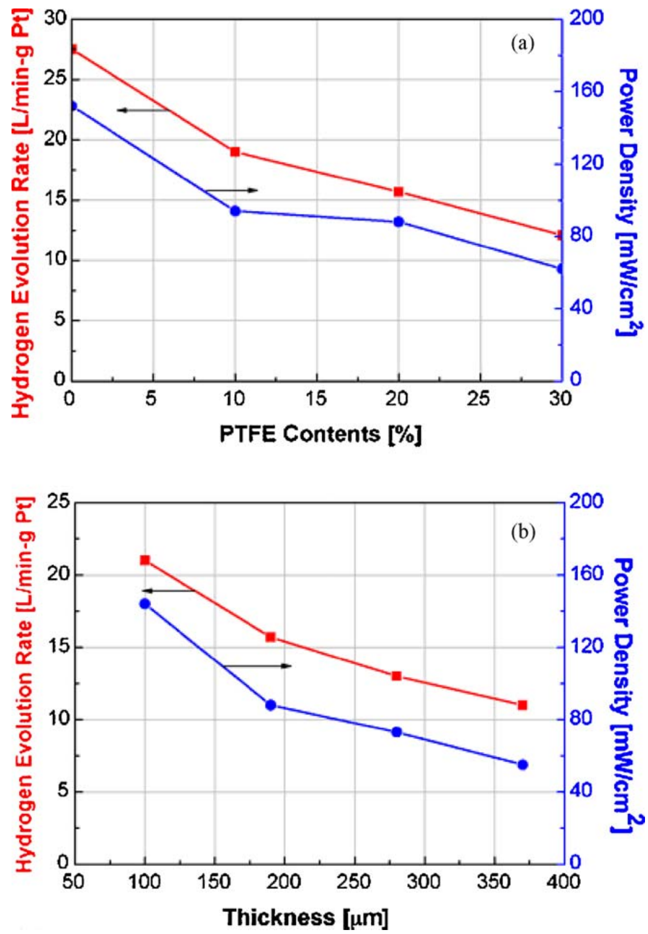


Fig. 7. Hydrogen evolution rate and power density for DBFCs, which employ carbon-supported platinum as both anode and cathode catalysts and Nafion®-115 membrane as electrolyte, as a function of (a) PTFE content and (b) thickness of anode diffusion layers.From Ref. [51].

media for the reactant and product to flow, acts as a base substrate for deposition of catalyst layer, and manages water in the electrode. Typically, porous carbon paper and carbon cloth with different polytetrafluoroethylene (PTFE) contents and thicknesses are employed as the DL. A PTFE coating makes the DL water-proof and facilitates the release of gases. However, PTFE being hydrophobic in nature is undesirable for diffusion of aqueous solutions. A PTFE content of 15% and a thickness of 50 μm in both anode as well as cathode DLs were found to give the best performance in PEFCs [71]. Neergat et al. [72] studied the effect of DL morphology on the performance of DMFCs and found that Ketjen Black carbon yielded better performance than Vulcan XC-72 and acetylene black carbons in the DL. The authors further observed that DMFCs with hydrophilic DL on the anode and hydrophobic DL on the cathode gave better cell performances. A PTFE content of 30 wt.% in anode DL gave the most stable behavior in DMFCs [73].

DL of DBFCs shares similarities with those of PEFCs and DMFCs, but there are differences also. Park et al. [51] investigated the influence of anode diffusion layer properties on the performance of DBFC. It was found that with decrease in the content of PTFE binder in anode diffusion layer, both the rate of hydrogen evolution and power density of DBFC increased as shown in Fig. 7(a). In DBFCs, aqueous liquid transportation is more significant than gas transportation, since hydrogen bubbles generated in the anode can be released through the DL even if pathways for gas transportation are not formed, while the viscous alkaline $NaBH_4$ solution will find it difficult to diffuse through DL without wet-ability. Thinner layers were found to give better performance as shown in Fig. 7(b) due to their effectiveness in promoting fuel diffusion and releasing hydrogen gas. Thus, a thin DL with a high level of wet-ability is desirable for DBFC anodes.

4. Membrane

Cathode electro-catalysts such as Pt are active toward borohydride electro-oxidation and hence, it is necessary to keep the fuel from crossing over to the cathode while allowing the transport of ions [70]. Membranes can be evaluated in terms of many properties, such as conductivity, composition, thickness, mechanical strength, equilibrium water content (EWC), and ion exchange capacity (IEC) values. In DBFC, it is necessary to balance the water content, since membrane hydration is essential to maintain proton conductivity whereas excess water leads to flooding [39]. It is also worthwhile to consider the effect of temperature on membrane. Increase in temperature increases membrane conductivity and therefore enhances power density [23]. However, increased temperature also leads to dryness within the membrane and poor water balance inside the cell, which results in higher resistance and decreased cell performance [74].

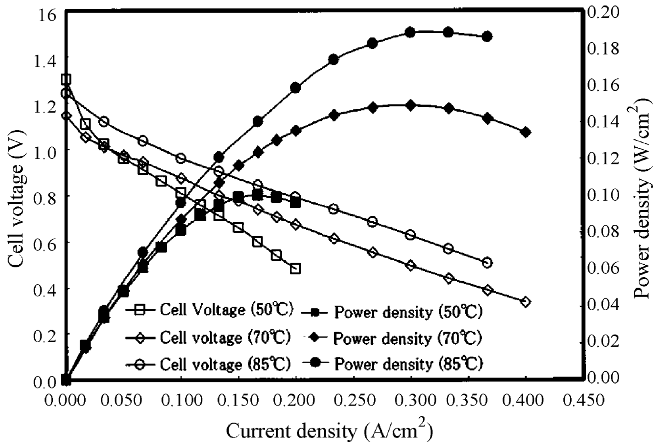


Fig. 8. Cell performance curves for DBFC consisting of $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ alloy as anode, carbon-supported platinum as cathode, Nafion®-117 membrane as electrolyte operating with 10 wt.% aqueous $NaBH_4$ in 20 wt.% aqueous NaOH solution as fuel and humidified oxygen as oxidant at 50, 70 and 85 °C.From Ref. [6].

Membrane stability under fuel cell operating conditions exerts a large effect on the lifetime and cost of MEAs. Both anion exchange membrane (AEM) and cation exchange membrane (CEM) serve this purpose to a great extent. AEMs allow efficient transport of OH^- from cathode to anode compartment, but suffer from the problem of BH_4^- crossover. Compared to AEM, use of CEM greatly alleviates the effect of borohydride crossover. Besides, CEMs are commercially available and among them the perfluorinated membranes specially show good ion conductivity, chemical and mechanical stability [70,75]. Nafion® membranes are a kind of CEMs that was first employed in DBFC by Li et al. [25] and is still employed in a majority of DBFCs [23,70,76,77]. Cell performance curves for borohydride-oxygen fuel cell consisting of $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ alloy as anode, carbon-supported platinum as cathode, Nafion®-117 membrane as electrolyte at different temperatures are shown in Fig. 8. These membranes rely on water for the proton conductivity and therefore, are preferably operated at temperatures below 90 °C. Nafion® membranes show lower ionic and interfacial resistances and therefore higher power density than AEMs as shown in Fig. 9 [70]. In DBFC, the sodium ion is transported through the Nafion membrane instead of hydrogen ion as in the case of hydrogen-based PEFC. Na^+ has larger size than H^+ and so it is expected that the ion transport resistance is larger for the DBFC than the hydrogen PEFC [70]. Prior to assembly, the Nafion membranes are pretreated by boiling in H_2O_2 solution to remove the remaining contaminants [51].

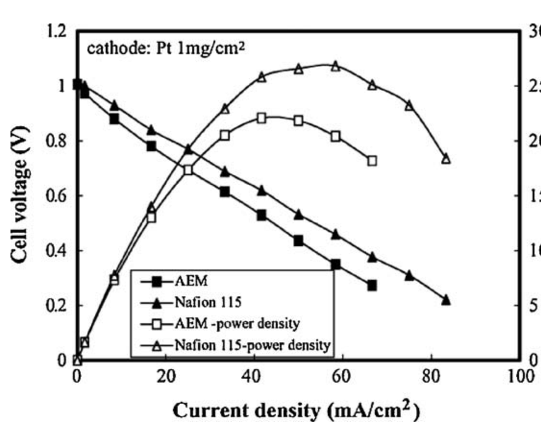


Fig. 9. Cell performance data for DBFCs, which employs porous nickel as anode catalyst, carbon-supported platinum as cathode catalyst and an anion exchange membrane as well as Nafion®-115 cation exchange membrane as electrolytes, operating at ambient temperature in an air-breathing mode.From Ref. [70].

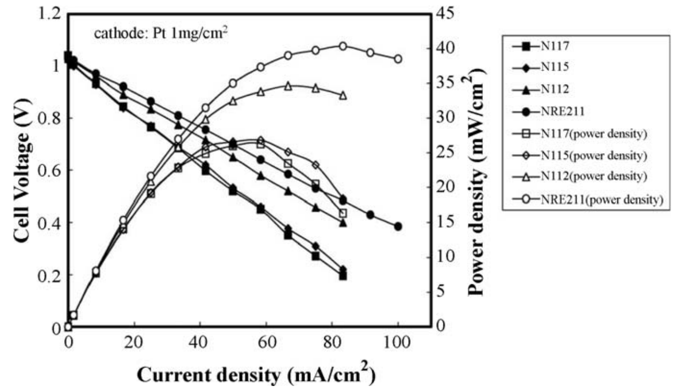


Fig. 10. Cell performance curves for DBFCs, which employs porous nickel as anode catalyst, carbon-supported platinum as cathode catalyst and Nafion membranes with various thicknesses as electrolytes, operating at ambient temperature in an air-breathing mode.From Ref. [70].

Without the pretreatment, the membrane induced lower and less stable voltage compared to the pretreated membrane [36]. Thickness is a major factor in determining the effectiveness of membranes. DBFCs with thin membranes show low ohmic resistance and charge transfer resistance. Reduction in membrane thickness leads to improvements in power density despite the increase in borohydride ion crossover [70] as shown in Fig. 10.

The problem with the usage of CEMs in DBFC is that it would reduce alkali concentration in the anolyte, which causes instability and inefficient use of the borohydride. Moreover, the build up of alkali in the cathode associated with the use of CEMs as well as ORR results in the formation of carbonates in the presence of CO_2 in air, which deactivates the cathode as well as membrane and restricts flow of oxygen/air to the cathode. The problem becomes more severe in a longer operation and therefore a way to remove CO_2 and to return the NaOH from catholyte to anolyte is needed [68]. To reduce alkali crossover from anode to cathode in the cell, Nafion®-961 membrane was used instead of Nafion®-117. Nafion®-961 membrane is a Teflon-fiber reinforced composite membrane with sulfonate (100 μm thick) and carboxylate (10 μm thick) polymer layers. The carboxylate layer of Nafion®-961 membrane offers resistance to flow of NaOH from anode to cathode, thereby improving cathode polarization behavior of DBFC [78,79]. A comparison of cathodic polarization data for DBFCs employing Nafion®-117 and Nafion®-961 membranes as electrolytes is shown in Fig. 11.

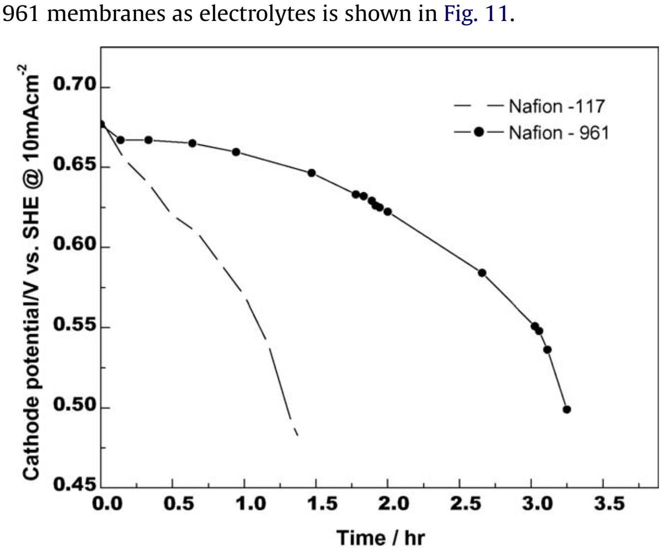


Fig. 11. A comparison of cathodic polarization data for DBFCs employing carbon-mixed Misch metal alloy $M_mNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ as anode, gold as cathode and Nafion®-117 and Nafion®-961 membranes as electrolytes.From Ref. [78].

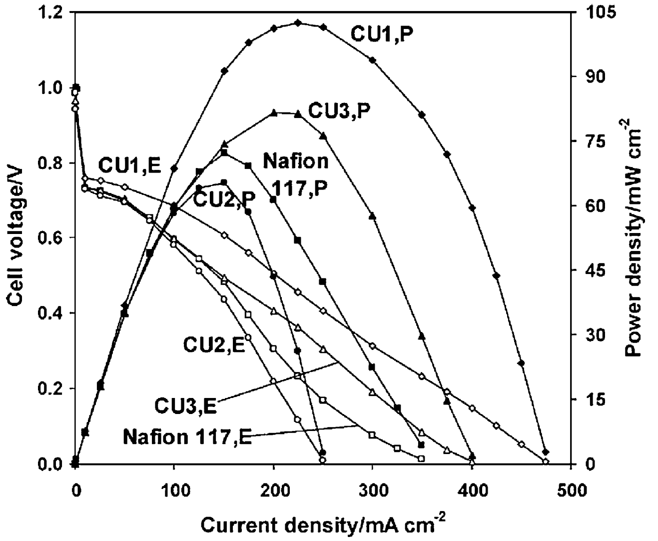


Fig. 12. Cell polarization data for DBFCs, recorded at a temperature of 85 °C, employing carbon-supported gold as anode, carbon-supported platinum as cathode, oxygen at ambient pressure as oxidant, and CU1, CU2, CU3 as well as Nafion®-117 membranes as electrolytes.From Ref. [80].

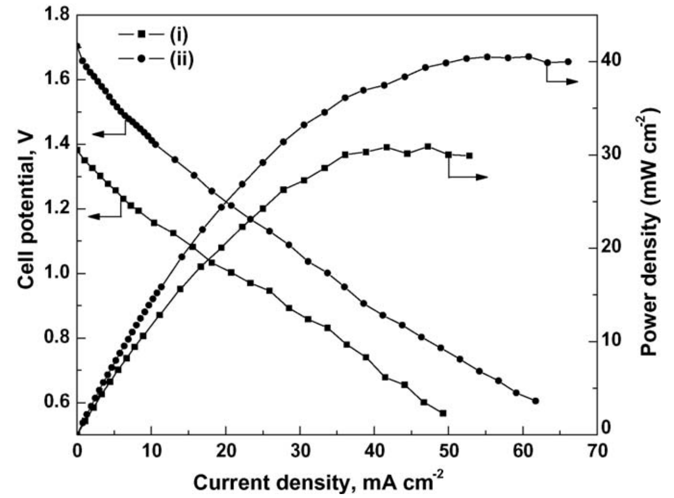


Fig. 13. Cell performance data for DBFCs employing an AB_5-type alloy of composition $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ as anode, gold-plated stainless steel mesh as cathode and (i) polyvinyl alcohol hydrogel, as well as (ii) Nafion®-117 membranes as electrolytes.From Ref. [82].

Cheng et al. [80] prepared several ion exchange membranes (CU1, CU2, CU3) by radiation grafting technique and evaluated them in DBFCs. CU1 membrane fabricated by grafting styrene onto polyethylenetetrafluoroethylene followed by a subsequent sulphonation reaction gave the highest power performance in DBFC among all the new membranes investigated in the research presented in this paper. The said membrane also yielded better performance than Nafion®-117 membrane in DBFC due to its high ionic conductivity and high ion exchange capacity. However, this membrane did not show good stability in terms of peak power density. Cell polarization data for DBFCs, recorded at a temperature of 85 °C, employing CU1, CU2, CU3 as well as Nafion®-117 membranes as electrolytes are presented in Fig. 12. Cheng et al. [39] also made a comparison between Nafion®-117 and laboratory-made 3541P membrane, which consists of ethylene-tetrafluoroethylene (65%) backbone and polysulphonic acid (35%) grafting polymers. The 3541P ionomer membrane has higher IEC, EWC, and ionic conductivity and therefore, gave better performance than Nafion®-117 membrane despite slightly lower OCV values. However, the 3541P ionomer membrane was unsuitable for application at elevated temperatures (e.g. 70 °C), despite its good stability at ambient temperature. Lakeman et al. [81] have studied various properties of a number of CEM electrolytes and employed them in DBFCs. The CEMs possessed properties comparable to those of Nafion®-112 and Nafion®-117 membranes.

Choudhury et al. [82] have reported a hydrogen peroxide oxidant-based DBFC with PVA hydrogel membrane as electrolyte and compared its performance with a similar DBFC employing Nafion®-117 membrane electrolyte. Without any auxiliary facilities such as peristaltic pumps, peak power densities of about 30 and 40 mW cm^{-2} have been observed for the DBFCs with polyvinyl alcohol hydrogel and Nafion®-117 membrane electrolytes respectively at ambient temperature as shown in Fig. 13(i) and (ii). The nominally better cell performance of the Nafion®-117 based DBFC could be due to the higher ionic conductivity of Nafion®-117 (10^{-1} S cm^{-1}) than PVA hydrogel membrane (10^{-2} S cm^{-1}) [82].

Finally, it should be noted that operating a DBFC without a membrane or any other separator will simplify the engineering aspects. In order to achieve this, some researchers have used cathodes that are inactive towards electro-oxidation and chemical hydrolysis of BH_4^-. Such cathodes include the above mentioned materials such as manganese oxide [57], iron tetramethoxy phenyl porphyrin [55,66], iron phthalocyanine (FePc) [61], and cobalt phthalocyanine (CoPc) [60].

5. Operational parameters of DBFCs

5.1. Anolyte component and concentration

The anolyte used in DBFC consists mostly of $NaBH_4$ in NaOH or KOH aqueous solution. Alkaline medium is used in anolyte as high concentration of OH^- stabilizes BH_4^- by hindering its hydrolysis. Borohydride concentration is an important factor in determining DBFC performances. Effect of $NaBH_4$ concentration on the performance of DBFC has been reported in the literature [23,50,74,83]. It has been observed that increase in $NaBH_4$ concentration improves power density and sustained current density of DBFC by enhancing mass transfer of the fuel and kinetics of borohydride electro-oxidation. At the same time, borohydride crossover and hydrolysis are also enhanced with increased BH_4^- concentration, which results in the platinum cathode performance deterioration, fuel loss, and decrease in the OCV [74].

Alkali concentration in anolyte also affects the DBFC performance. However, this effect has been found to be relatively small as compared to the effect of BH_4^- concentration [74]. Increasing NaOH concentration up to 10% has been found to be beneficial for DBFC performance in terms of enhanced OCV, power density, and sustained current density beyond which a negative effect is observed [74]. Increasing NaOH concentration has the positive effects of improving anode reaction, increasing the conductivity of the sodium hydroxide solution and reducing possible borohydride hydrolysis [74,83]. Yet, increased NaOH concentration has negative effect to cathode reaction and also leads to an increase in solution viscosity which decreases the movability of borohydride ions and sodium ions in the anode catalyst layer [74,83]. Increase in NaOH concentration also results in the formation of sodium carbonate in the presence of atmospheric CO_2 [74].

Overall, both $NaBH_4$ and NaOH concentrations need to be optimized for the borohydride stability, DBFC performance and cost. In most studies on DBFCs, it has been found that optimum concentrations of $NaBH_4$ and NaOH range between 10 and 30 wt.% and between 10 and 40 wt.%, respectively [76]. Optimum concentrations of $NaBH_4$ and NaOH in DBFC anolyte have been found to be 10 and 20 wt.% respectively [6,23,84].

5.2. Anolyte flow rates

High fuel flow rate improves mass transport of the fuel, eliminate probable channel blocking and product accumulation, thereby improving the DBFC performance [74]. Studies carried out by Duteanu et al. [83] found that increasing fuel flow rate has only limited influence on the performance of anode polarization, cell polarization, and power density of DBFCs. The authors opined that although the increase in fuel flow rate promotes mass transport of BH_4^-, the improvement in DBFC performance is expected to be very small since the major transport resistance would be in the catalyst layer where convective transport effects are mainly absent. The same authors emphasized that an increase in fuel flow rate may result in the development of a high pressure in the anode compartment, which will force more anolyte and hence more BH_4^- to crossover to the cathode compartment, thereby adversely affecting the DBFC performance. Considering the relatively small influence of fuel flow rate on DBFC performance, it would be more economic to use low flow rates [74].

5.3. Anolyte additives

Hydrogen evolution arising from the hydrolysis of BH_4^- in DBFC results in low fuel utilization efficiency. One of the ways to overcome this limitation is to add some materials that are known for their inhibiting effect on hydrogen evolution to the BH_4^- solution. It was found that addition of thiourea (TU) into anolyte of DBFC minimizes the catalytic hydrolysis of BH_4^- and electro-catalytic evolution of hydrogen by poisoning the active sites of hydrogen adsorption and therefore, improves the BH_4^- utilization and coulombic efficiencies [15,38,85]. However, TU is a sulphur containing organic compound that on decomposition generates sulphur, which is a poison for metallic sites of catalysts employed as DBFC anodes [86,87] and leads to drastic decrease in fuel cell performance [38]. Jamard et al. [38] concluded that instead of adding thiourea in the fuel solution, it is better to optimize the anodic mass loading to achieve both high values of fuel utilization efficiency and power density.

5.4. Catholyte

The oxidant of the DBFC can be oxygen, air, or hydrogen peroxide. Although DBFCs using air do not yield better performance than those using oxygen, it is desirable to develop a DBFC with air as oxidant simply because it is available freely in nature. Use of pressurized oxygen has been reported [74] to exhibit to better DBFC performance due to improved cathode kinetics resulting from enhanced oxygen supply.

Miley et al. [48] observed that the use of H_2O_2 as oxidant in DBFC results in more than 30% higher output voltage as compared to PEFCs employing hydrogen and oxygen as fuel and oxidant, respectively. The benefits of using hydrogen peroxide as the oxidant in fuel cells especially for space power applications have been well analyzed in the literature [48,88]. Hydrogen peroxide being liquid at ambient temperature possesses higher volumetric energy density as compared to gaseous oxygen as oxidant [88]. Storage, transportation, and usage of H_2O_2 are easier as compared to gaseous oxygen due to its liquid nature at room temperature. These features of H_2O_2 simplify engineering aspects and enhance compactness of the DBFC, thereby bring down the cost significantly. From the kinetics point of view, electro-reduction of H_2O_2 involves two electrons and hence has a lower activation energy barrier as compared to oxygen reduction, which is a four electron transfer process [48]. This implies a higher reaction rate for electro-reduction of H_2O_2 as compared to O_2. Also, H_2O_2 being a liquid avoids accumulation of alkali in the cathode pores and subsequent carbonate fouling in DBFC [23]. In contrast to O_2-based DBFC, H_2O_2-based DBFC has a higher efficiency due to its single-phase transport within the cell [48]. Moreover, OCP value of O_2-based DBFC is 1.64 V whereas the same for H_2O_2-based DBFC varies between 2.11 and 3.02 V, depending on the pH of the catholyte. Usage of H_2O_2 enables DBFC to operate in anaerobic locations, such as underwater and in space. However, H_2O_2 has the disadvantage of decomposition when metals such as Pt, Pd, and Au are used as cathodes [77]. Therefore, appropriate cathode materials need to be developed that would promote the direct electro-reduction of H_2O_2 while eliminating the decomposition of H_2O_2.

The performance of H_2O_2-based DBFC relies highly on temperature, concentration, and pH value of hydrogen peroxide. A higher power density is achieved when pH was moved from 1 to 0 as shown in Fig. 14 [24] and the power density may change by 25 mW cm^{-2} with peroxide concentration [23] as shown in Fig. 15. $NaBH_4$–H_2O_2 fuel cell is cathode-limited as indicated by the anode and cathode polarization data for a DBFC operating with $NaBH_4$/NaOH fuel and hydrogen peroxide oxidant as shown in Fig. 16. Direct borohydride–H_2O_2 fuel cells achieving peak power density values as high as 680 mW cm^{-2} at 60 °C and 1.5 W cm^{-2} at 65 °C have been reported by Gu et al. [65] and Luo et al. [89], respectively. It may be noted that H_2O_2 is not a suitable oxidant in DMFC until a membrane is developed that completely prohibits methanol crossover from anode to cathode chamber. This is because methanol being a small organic molecule and soluble in water will crossover across any polymer membrane electrolyte separator and will undergo direct combustion reaction with H_2O_2 resulting in generation of a large amount of heat, which will make it difficult to operate the DMFC at a controlled temperature.

5.5. Effect of temperature

Cheng et al. [74] studied the effect of temperature on the performance of DBFC and observed that increase in temperature has both beneficial as well as detrimental effects on the DBFC performance. Enhancement of temperature improves diffusion coefficients and mass transfer of the reactants, increases kinetics of electro-oxidation of BH_4^-, and electro-reduction of the oxidant as also the ionic conductivity of anolyte and catholyte, all of which result in an increased power and sustained current densities of DBFC. To the contrary, increase in temperature results in an increase in the rate of crossover and hydrolysis of BH_4^-, which results in a decrease of fuel utilization efficiency and affects the electro-catalytic activity of the cathode that is manifested in the decrease of OCV of the DBFC. Unlike PEFC, DBFC being a liquid-based fuel cell, may not experience the detrimental effect of drying of membrane as a result of increased temperature.

Generally the detrimental effects of increased temperature are outweighed by the beneficial effects on DBFC performance as indicated by the overall four fold increase in power density of DBFC with an increase of temperature by 60 °C [74]. Moreover, the DBFC can work in a wide range of temperature and exhibits a reasonably good power density and energy capacity even at ambient temperature, which satisfies the necessary conditions for portable applications.

6. Fuel cell configuration and fuel cell systems

6.1. Single fuel cell

The main component of a DBFC is membrane electrode assembly (MEA) that consists of either an anion or a cation exchange membrane sandwiched between the two electrodes. The anode and cathode of the MEA are contacted on their rear with fluid flow field plates machined from high-density graphite or

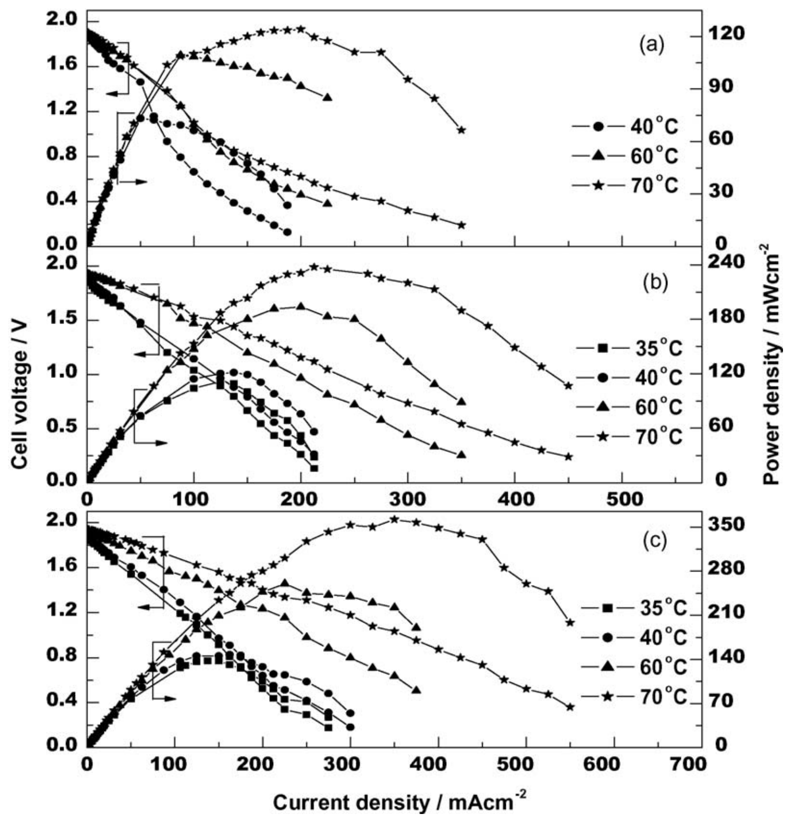


Fig. 14. Cell polarization data for DBFCs employing Nafion®-117 membrane as electrolyte operating at temperatures between 35 and 70 °C with optimized solution of aqueous alkaline $NaBH_4$ fuel fed at $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy anode and 15% w/v H_2O_2 oxidant solution of (a) pH ≈ 1, (b) pH ≈ 0.5, and (c) pH ≈ 0 fed at the carbon-supported platinum cathode.From Ref. [24].

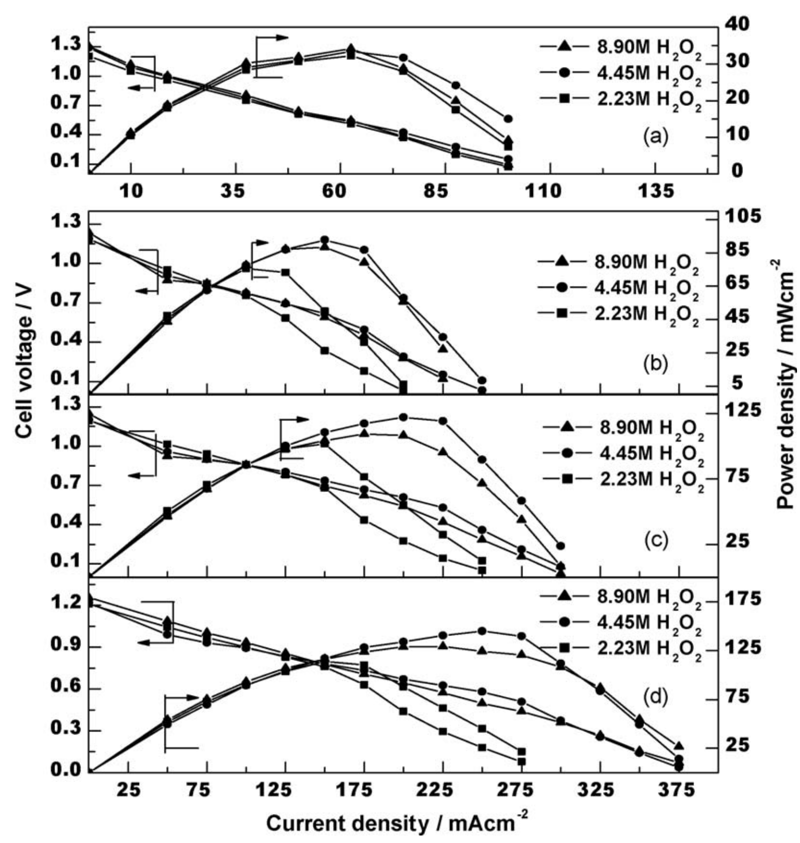


Fig. 15. Galvanostatic polarization data for DBFC comprising Nafion®-117 membrane as electrolyte with alkaline $NaBH_4$ fuel of optimized concentration fed at the $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy anode and varying concentrations of hydrogen peroxide fed at the carbon-supported platinum cathode at (a) 30 °C, (b) 50 °C, (c) 60 °C, and (d) 70 °C.From Ref. [23].

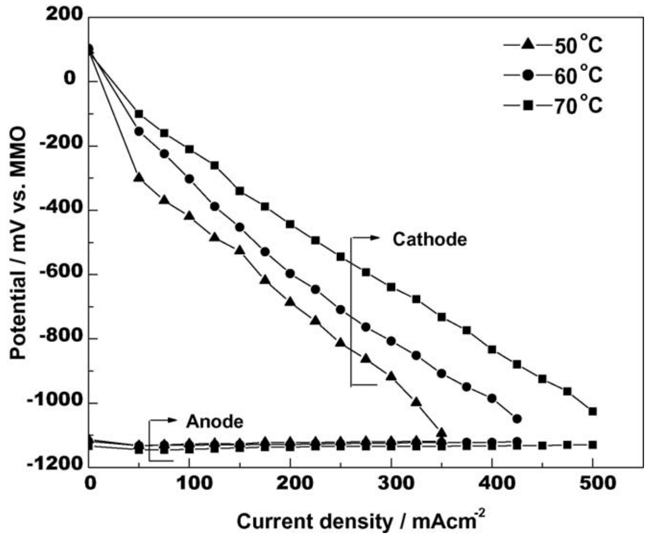


Fig. 16. Anode and cathode polarization data for a DBFC comprising $M_mNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ alloy as anode, carbon-supported platinum as cathode, Nafion-117 membrane as electrolyte operating with optimized concentrations of fuel consisting of a solution mixture $NaBH_4$ and NaOH and hydrogen peroxide oxidant at 50, 60 and 70 °C.From Ref. [23].

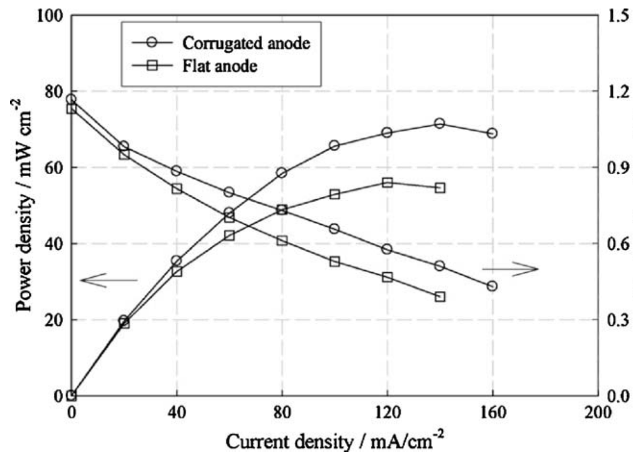


Fig. 17. Performance data for DBFCs employing carbon-supported platinum as cathode, Nafion®-115 membrane as electrolyte and fluorinated Zr-based AB_2-type hydrogen storage alloy in flat and corrugated forms as anodes with fuel inlet and air inlet temperatures of 60 and 45.5 °C respectively.From Ref. [90].

stainless steel blocks in which channels are machined to achieve minimum mass-polarization in the DBFC. The ridges between the channels make electrical contact to the rear of the electrode and conduct current to the external circuit. The channels supply alkaline sodium borohydride solution to the anode and oxygen, air, or hydrogen peroxide to the cathode. Electrical heaters are generally placed behind each of the graphite blocks to heat the cell to a desired temperature. Fuel consisting of a solution of sodium borohydride in aqueous sodium hydroxide is pumped into the anode chamber through a peristaltic pump and oxidant consisting of oxygen, air, or hydrogen peroxide is introduced into the cathode chamber either through a mass flow controller or a peristaltic pump. The graphite blocks are also provided with electrical contacts and tiny holes to accommodate thermocouples. Usually a pre-treated Nafion® ionomer membrane is hot-pressed together between two the electrodes to fabricate an MEA. However, Liu et al. [70] prepared MEA for DBFC by simply pressing the anode, membrane, and cathode together so as to make mechanical contact between membrane and the electrodes. The authors noted that it is beneficial to leave some space between the anode and the membrane so that fuel would contact the anode more completely and also hydrogen would be released from the anode more freely. In a DBFC stability test, the cell using an anode tightly pressed onto the membrane encountered a quick decrease in cell voltage compared to the cell with the anode apart from the membrane [36]. Kim et al. [90] also remarked that since Na^+ ions can easily be transferred through the liquid fuel, a close contact between the anode and membrane is not necessary. To further facilitate the removal of hydrogen bubbles trapped in the gap between the membrane and the anode, they adopted a corrugated anode design, which had a 2 mm gap between the membrane and the anode. This anode design increased the DBFC performance by 27% as compared to a flat anode as shown in Fig. 17.

For portable direct liquid fuel cells, the current status of MEA morphology, flow-field designs, and fuel cell system architecture are surveyed by Qian et al. [91]. Proper design of flow field plates is important so that the distribution of reactants and transportation of products inside the fuel cell takes place smoothly. Different types of flow field designs have been investigated for application in PEFCs and DMFCs. Among them, serpentine flow field (SFF) and parallel flow field (PFF) designs are the most commonly used in direct liquid fuel cells. In principle, SFF facilitates mass transportation and reduce channel blocking more effectively than the PFF [92]. Cheng and Scott [74] achieved an increase of 3.5% in the peak power density of DBFC with SFF design in contrast to the PFF design at ambient pressure.

Fuel cell flow plates are usually made of graphite or stainless steel. Despite high corrosion resistance ability, stainless steel end plates are still vulnerable to galvanic corrosion. Therefore, a gold anti-corrosion coating is applied to the flow plate surface and is shown to improve cell performance by as high as 56% [90]. Coowar et al. [53] used QinetiQ's tubular cell design instead of the commonly used hot-pressing procedure for MEA fabrication, wherein the anode, membrane and cathode were placed around a perforated hollow stainless steel cylinder and clamped by a stainless steel grid. With air as oxidant, a power density as high as 28 mW cm^{-2} could be achieved at ambient temperature due to good electrode/membrane interface.

Pressurized oxygen or air is usually humidified before allowing it to enter the cathode chamber. Air or oxygen humidification exerts a positive influence on DBFC performance by reducing $NaBH_4$ accumulation on the cathode surface and also by preventing dryness of the membrane. For portable applications, passive conditions are required. Liu et al. reported [70] a micro DBFC with a fuel tank attached to the end-plate and an air-absorbing cathode. The cell exhibited a peak power density of 40 mW cm^{-2} without the presence of any auxiliary facilities. Liu et al. reported [34] enhancement of DBFC single cell performance by adding carbon-supported Pd and Nafion ionomer to nickel-based anode. A power density as high as 80 mW cm^{-2} was achieved at ambient conditions without using any pump and other auxiliary accessories.

6.2. Fuel cell stack

To boost the power output, a number of individual cells are connected to form a fuel cell stack. A commonly employed design of fuel cell stacks is the bipolar mode in which bipolar plates connect two cells electrically and at the same time supply fuel and oxidant to two adjacent cells. A general model for the calculation of pressure and flow distribution in fuel cell stacks has been proposed by Koh et al. [93]. A major problem with stacking is the increased possibility of pressure loss and reactant maldistribution. Hydrogen evolution particularly causes uneven fuel distribution in DBFC stack. Thus, proper design is needed to achieve uniform reactant distribution among cells. Liu et al. [54] implied that changing the fuel flow pattern in the stack could reduce the negative influence of

hydrogen evolution on stack performance. According to their study, divided parallel supply was shown to increase stack power compared to parallel supply. Yet further investigations are needed to explain the reason.

Another issue is weight minimization of fuel cell stacks. As in single cells, graphite can be used instead of stainless steel as bipolar plates to reduce stack weight, even though graphite has insufficient material strength to withstand the force for stack tightening. The stack weight was reduced by 4.2 times by using graphite bipolar plates and yet 12% of performance degradation was observed due to the insufficient stacking force [94]. Thus, when light materials are used as bipolar plates and endplates, a proper sealing system is necessary to achieve better contact with less stacking force [94].

It is also worthwhile to note that $NaBH_4$–NaOH fuel solution and hydrogen peroxide oxidant are conductive liquid with the conductivity on the order of 200 mS cm^{-1}. The conductivity of theses liquids cause short circuit and excessive corrosion problems to bipolar stacks [95]. To solve these problems, Luo et al. [95] applied a cell-isolation fuel distribution network (CIFDN) to $NaBH_4/H_2O_2$ FC which produced stack power in the kilowatt range.

Ponce de Léon et al. reported [77] H_2O_2-based DBFC with one, two, and four cells connected in a bipolar mode. The peak power densities obtained at 20 °C for two- and four-cell stacks were 25 and 37.5 mW cm^{-2} with cell voltages of 0.81 and 3.2 V at current densities of 16 and 12 mA cm^{-2}, respectively. Raman et al. reported [79] a 28 W direct borohydride/hydrogen peroxide fuel cell stack consisting of six single cells connected in series. A peak power-density of 50 mW cm^{-2} at an operating stack potential of 1 V was achieved at 25 °C. Li et al. reported [96] a single cell module and a five-cell stack employing a mixture of surface treated $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ Laves phase AB_2 alloy and Pd/C as the anode, carbon-supported platinum as the cathode, and Nafion® membrane (NRE-211) as the electrolyte. A peak power density of 290 mW cm^{-2} has been achieved for the single cell module of DBFC with air as oxidant at a temperature of 60 °C. The five-cell stack with effective area of 67 cm^2 exhibited a power of 110 W at 60 °C as shown in Fig. 18. Miley et al. [48] assembled a $NaBH_4/H_2O_2$ fuel cell stack, which generated a power of more than 500 W at a loading current of about 29 A and 17 V. Liu et al. [34] assembled DBFC stacks consisting of 2 and 8 cells in a planer design with simplified structures. A power density of 75 mW cm^{-2} and a net power of 2.5 W were achieved with 2 and 8 cell-stacks, respectively operated in a fully passive and air breathing mode.

7. DBFC performance and its durability

Performance of DBFC single cell depends on a large variety of factors such as materials for anode, cathode, membrane electrolyte, catalyst backing layer, fluid flow field, and operational parameters such as anolyte composition, anolyte pH, catholyte composition, catholyte pH, humidity of oxygen, temperature, and hardware component such as fluid flow-field pattern. In stacks comprising DBFC single cells, mode of stacking, overcoming maldistribution of reactants and difficulties arising from the evolution of hydrogen on the anode side and oxygen on the cathode side play pivotal roles in achieving high power performance in DBFC. Table 1 summarizes performance data for DBFCs employing metal anodes. Ponce de Léon et al. [76] opined that comparison of performance data for DBFCs is very difficult due to the differences in operating conditions chosen by different research groups.

A key to commercialization of DBFC is to demonstrate its reliability and long-term operation. Li et al. [6] showed that a DBFC using surface-treated Zr–Ni Laves phase AB_2 alloy as anode and Pt/C as cathode was able to operate stably for 29 h at 200 mA cm^{-2}

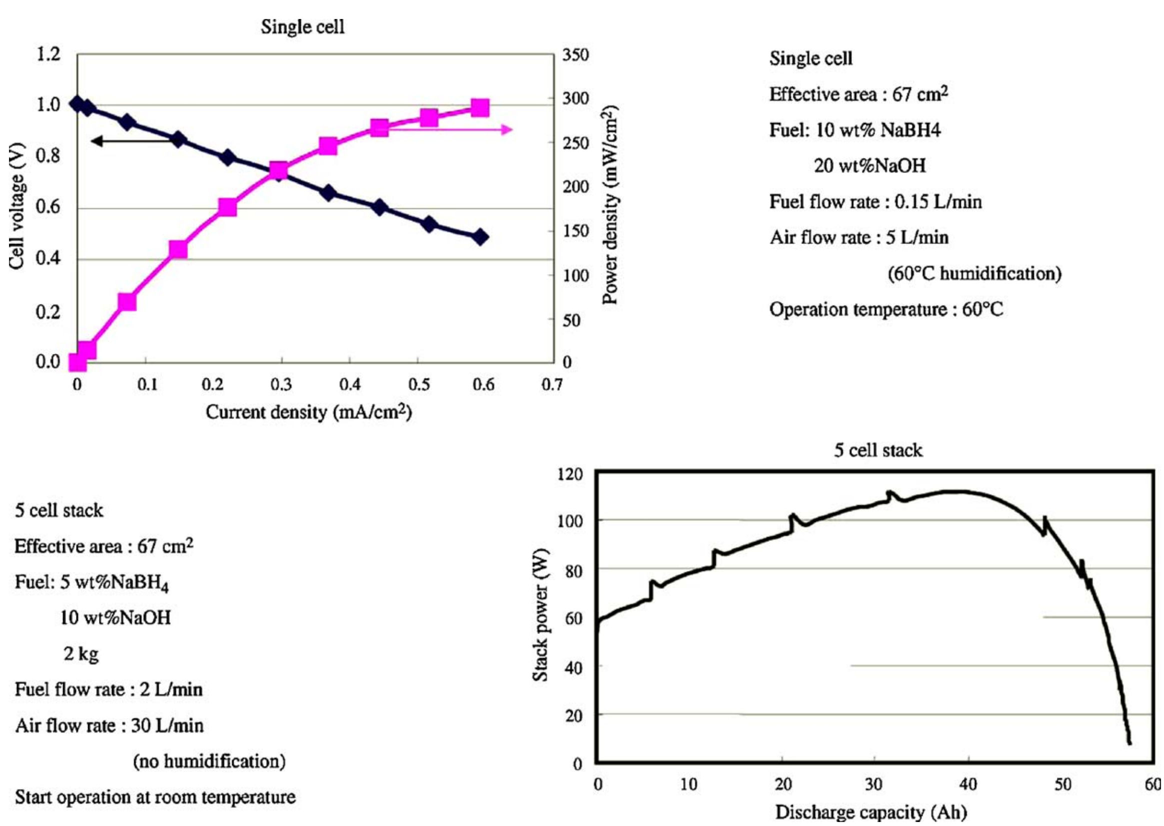


Fig. 18. Single and five-cell stack performances of the DBFCs employing a mixture of surface treated $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ Laves phase AB_2 alloy and carbon-supported palladium as anode, carbon-supported platinum as cathode and a Na^+ form Nafion® membrane (NRE-211) as the electrolyte.From Ref. [96].

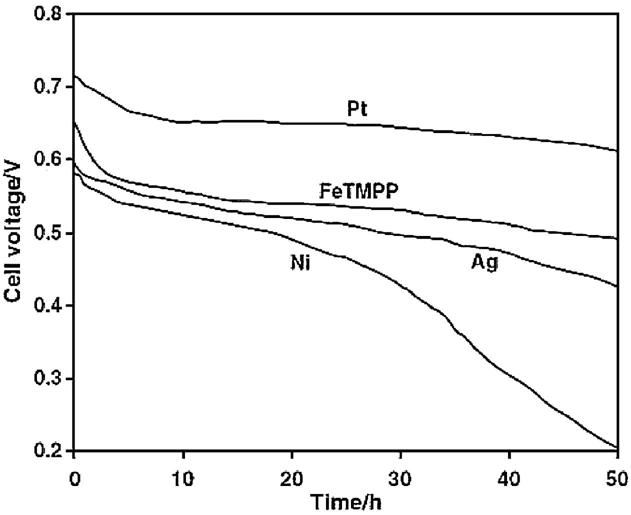


Fig. 19. Durability data for DBFCs employing carbon-supported platinum, iron tetramethoxyphenyl porphyrin, silver and nickel as cathodes, carbon-supported gold as anode, and Nafion®-117 membrane as electrolyte at a temperature of 70 °C under a load current density of 50 mA cm^{-2}.From Ref. [55].

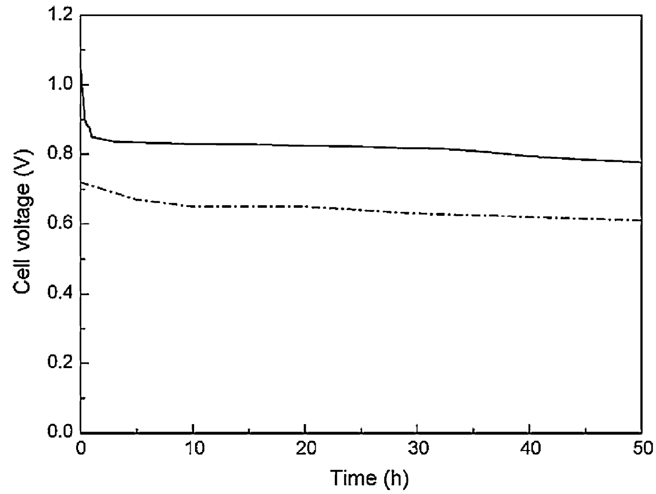


Fig. 20. Comparison of durability data of a DBFC employing misch metal-based AB_5-type alloy $M_mNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ as anode, carbon-supported iron phthalocyanin as cathode, oxygen as oxidant and no membrane electrolyte at ambient condition with that of a DBFC employing carbon-supported gold as anode, carbon-supported platinum as cathode, Nafion®-117 membrane as electrolyte and oxygen as oxidant at a temperature of 70 °C at a load current density of 50 mA cm^{-2}.From Ref. [61].

and 60 °C. Choudhury et al. [82] have reported a DBFC with PVA hydrogel membrane electrolyte that exhibited a nearly stable cell potential of about 1.2 V at a load current density of 10 mA cm^{-2} for about 100 h at ambient temperature.

Cheng and Scott [74] tested the performance stability of a borohydride-oxygen fuel cell using Au/C as the anode catalyst, Pt/C as the cathode catalyst and Nafion®-117 membrane by applying current density of 20 mA cm^{-2} at 25 °C. The DBFC maintained a relatively stable performance for 150 h. The authors attributed the gradual decline in the DBFC performance with time to factors such as changes in characteristics of catalysts, membrane, as also to supply and removal of fuel and oxidant. Crossover and hydrolysis of BH_4^- might also contribute to the limited durability of DBFCs. Cheng et al. studied the stability of various carbon supported metal electrodes and found that the Au/C and Pt/C anodes had higher stability than the Ag/C, Ni/C, and Pd/C during DBFC operation and the stability of Pt/C and Ag/C cathodes were found to be better than that of Pd/C and Ni/C cathodes [39]. A comparative study of the stability of carbon-supported FeTMPP, Ag, Ni, and Pt as cathodes for DBFC was made by Cheng and Scott [55] by monitoring DBFC voltage for 50 h of operation. Fig. 19 shows the durability data for DBFCs employing carbon-supported platinum, iron tetramethoxyphenyl porphyrin, silver, and nickel as cathodes, carbon-supported gold as anode, and Nafion®-117 membrane as electrolyte at a temperature of 70 °C under a load current density of 50 mA cm^{-2}. It was shown that the DBFCs with FeTMPP, Ag, and Pt cathodes exhibited comparable stabilities while the DBFC with Ni cathode exhibited poor stability. Ma et al. [61] tested the short-term stability of DBFC employing iron phthalocyanin as cathode catalyst by applying 50 mA cm^{-2} for 50 h at ambient atmosphere and found that both the open circuit potential and steady cell potential were higher than that using Pt cathode at 70 °C reported by Cheng and Scott [55]. Comparative results of voltage vs. time curves are shown in Fig. 20. The authors observed a decay in cell voltage of 5% during a test of 50 h and pointed out that it was due to the reduced effective porosity of the gas diffusion electrode and therefore poorer reactant transport, resulting from the formation of carbonate and water.

Cheng and Scott [68] carried out a comparative study on the durability of titanium mesh-supported gold and silver anodes in relation to carbon-supported gold and silver anodes in DBFCs. The authors observed that titanium mesh-supported anodes possessed better stability as compared to carbon-supported anodes in DBFCs. However, the performances of all the DBFCs gradually declined with time because of dissolution and agglomeration of anodes, poisoning of catalyst surfaces, deactivation of cathodes and membrane due to formation of a layer of NaOH and Na_2CO_3.

8. Cost factor in research and development of DBFC

According to an analysis by Wee [97], the total operating cost of DBFC systems are higher than those of DMFC systems; the DBFC system is relatively uneconomic at higher power outputs and longer operation times, but is more favorable in specific portable applications such as micro-power with shorter operational time spans. The high cost of DBFCs comes from the precious metal-based anode and cathode catalysts, sodium borohydride, and the membrane electrolyte [47]. Therefore, solutions to reduce cost are to modify catalyst materials for the anode and cathode, reduce the cost of $NaBH_4$, and produce cost-effective membrane [47]. It will be ideal to do away with membrane electrolyte separators and instead use cathode catalysts that have little reactivity towards electro-oxidation of BH_4^-. It was pointed out that the DBFC will be a powerful competitor in various applications of fuel cells if the cost of borohydride production can be reduced [98].

9. Summary and future directions

Various important aspects of DBFC such as electrochemical reactions that take place in anode and cathode, anode materials, cathode materials, electrolyte membrane separators, operational parameters, such as anolyte, catholyte, effect of temperature on performance, cell assembly modes, etc. are discussed. While electro-oxidation of BH_4^- takes place in alkaline medium yielding a high anode potential, hydrolysis of BH_4^- causes loss of fuel and hence is a hurdle in commercialization of DBFC. Mechanism of electro-reduction reaction taking place at the cathode can be altered by changing the pH of the catholyte, which gives an opportunity for obtaining a very high electrochemical cell potential of DBFC. Electro-reduction of oxygen and hydrogen peroxide is relatively a complicated process as compared to electro-oxidation of BH_4^-. Cathode potential polarizes much faster than anode potential, which makes DBFC a cathode-limited fuel cell. Both electro-oxidation of BH_4^- and electro-reduction of

oxidant take place on a large variety of precious and non-precious materials providing a low-cost route for developing an economically viable DBFC. DBFCs can be assembled with ionomer as well as non-ionomer membranes. Among ionomer membranes, both CEM and AEM have been employed to yield high performance even under ambient conditions because of high single electrode potentials. Crossover of BH_4^- from anode to cathode through the membrane electrolyte results in loss of fuel and inefficient utilization of the oxidant, thereby adversely affecting DBFC performance. Development of low-cost polymer membranes with little BH_4^- crossover is a key in bringing DBFC to the level of common usage. Gas evolution resulting from hydrolysis of BH_4^- in anode and decomposition of H_2O_2 in cathode compartments has been found to pose a significant difficulty in assembling DBFC multi-cell stacks. Stability of DBFC single cell and stack performances have been reported for relatively shorter periods as compared to PEFC and DMFC. Cost of borohydride compounds is very high and it needs to be decreased significantly to make DBFC commercially viable.

In spite of the rapid growth in DBFC research, it is still at its infant stage and many problems remain to be solved. Novel anode catalysts need to be developed to depress hydrogen evolution and make the electro-oxidation of BH_4^- an eight or near eight-electron process. Efficient and cost-effective catalysts need to be developed to make electro-reduction of oxygen and hydrogen peroxide an efficient process with little decomposition of H_2O_2. Crossover of BH_4^- can be solved by developing membrane electrolytes with high BH_4^- resistivity and cathode catalysts with high selectivity for electro-reduction of oxidant and high tolerance towards borohydride electro-oxidation. One of the solutions to reduce high DBFC cost lies in the cost reduction of sodium borohydride. DBFCs share similarities in terms of electrode preparation methods, fuel cell system design, etc. with PEFCs and DMFCs, which have been developed in more depth, and therefore, the knowledge obtained from research into these fuel cells can be used to guide investigations into DBFC research. In addition, the electrode and electrolyte materials used in other electrochemical devices such as batteries, electrochemical supercapacitors, electrochemical sensors, etc. can also be considered for application in DBFC. Besides, since DBFCs are the most attractive in portable applications, more research efforts need to be carried out toward making DBFCs miniaturized and lightweight.

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